THE RATE OF LOSS OF DISSOLVED ORGANIC CARBON (DOC) THROUGH A CATCHMENT

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Abstract

Given observed trends in the concentration of DOC in surface waters in northern hemisphere the degradation of DOC to CO_2 could represent a major and increasing source of greenhouse gas to the atmosphere. However, studies of DOC turnover in rivers have been predominantly based upon mass balance studies and empirical studies have focused upon lakes and estuaries which have far longer residence times than would be the case for transit via rivers. The study measured DOC loss in unfiltered river water samples across an 818 km^2 catchment every month for a year and considered total loss, photo and aphotic degradation as well as the rates of each process. The study found:

i) Rate of total DOC change in daylight varied from loss of 30.1 mg C/l/day to an increase of 3.5 mg C/l/day: the average loss was 73% over 10 days.

ii) Rate of change due to photic processes varied from decrease of 19.4 mg C/l/day to an increase of 6 mg C/l/day, i.e. net photo-induced production was possible.

iii) Activation energy of the degradation was estimated as 2.6 ± 1.2 kJ/gC.

iv) The apparent quantum yield varied from 9.6 and -1.7 mmol C/mol photons.

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v) Coupling models of total loss of DOC with estimates of in-stream residence times showed that annual loss rates of DOC across the 818 km^2 catchment would be between 48 and 69%, in line with estimates from mass balance studies, implying that in-stream DOC degradation represents a large, indirect source of CO_2 emissions from peats and other organic soils.

vi) Annual rate of removal was increasing in line with increasing loss of DOC at source, implying that observed DOC trends are leading to increased CO_2 emissions.

Introduction

The flux of dissolved organic carbon (DOC) from the terrestrial biosphere to the world's oceans has now been widely recognised as an important component of terrestrial carbon budgets particularly from highly organic soils, e.g. peats (Aitkenhead et al., 2007). Several attempts have been made to estimate the flux of DOC from the terrestrial biosphere. Meybeck (1993) estimated that the global river flux of DOC was 200 Mtonnes C/yr. Ludwig et al (1996) used a spatially-explicit model of global fluvial C fluxes to obtain an estimate of 400 Mtonnes C/yr, with a split of approximately 40:20:20 for DOC:POC:DIC. Harrison et al. (2005) estimated global river flux of DOC as 170 Mtonnes C/yr. For individual environments the export of DOC varies considerably: for lowland arable environments estimates of 0.9 and 1.9 tonnes C/km^2/yr have been reported (Royer and David (2005), Dalzell et al. (2007)); for lowland grassland 0.8 and 5.5 tonnes C/km^2/yr (Don and Schulze, 2008); and for forested sites of between 1.5 and 5.3 tonnes C/km^2/yr (Hope et al., 1997). Worrall et al. (2012) gathered information from 33 peat-covered catchments (all less than 40 km^2) from across the UK and found DOC export varied from 10.3 to 95.6 tonnes C/km^2/yr. Most studies calculate flux of DOC at the outlet of catchments, which may range from < 1 km^2 to 818 km^2. In general the rivers can be considered conduits rather than sources of DOC, since in-stream

(autochthonous) production is commonly low in peat streams relative to the soil source (Eatherall et al., 2000). By calculating the flux at the river output, the calculation ignores any processing that may have occurred prior to that point. Loss of DIC through degassing of CO_2 from lakes, reservoirs and streams can represent an exceptionally high loss of terrestrial C. Kempe (1982, 1984) recognised that many surface freshwater bodies were saturated with respect to CO_2 and would therefore be sources of CO_2 to the atmosphere. Not only is dissolved CO_2 lost in transit within the river system, but DOC will also be mineralised within the river system from its source to the river outlet (Richey et al. 2002): there will also be the possibility of autochthonous production of DOC within the river network although in peat covered catchments it is generally found to be not as great as the amount of allochthonous DOC (Eatherall et al., 2000). Therefore measuring DOC flux solely at the river outlet provides a likely underestimate of the loss of carbon (and therefore greenhouse gas emissions) from the terrestrial biosphere. Cole et al. (2007) have estimated that at a global scale 1.9 Pg C/yr enters rivers of which 0.8 Pg C/yr (42% of the input) is returned to the atmosphere, while Battin et al. (2009) suggested a lower limit of 21% removal of DOC in-stream. The IPCC now include an estimate of global DOC flux (Solomon et al., 2007) but do not yet consider any losses of DOC in-stream and so this flux value has no direct impact upon atmospheric greenhouse gases.

In-stream processing of DOC and POC is often referred to or invoked as an explanation or implication of the research in the literature, but is rarely quantified. Within streams there are a range of processes that could remove, degrade or add DOC to the flux (Fig. 1). The concept of the river spiralling and the continuum (Newbold et al., 1982) deals with the fate of all carbon (and nutrients) within a river system, but does not address the fate of individual components of the total carbon flux. However, in-stream fauna can utilise DOC and biodegradation interacts with light to speed up degradation (Moran and Zepp, 1997). The

stream fauna and flora have the potential for autochthonous DOC production and autochthonous DOC has been reported as less prone to biodegradation and less prone to photosensitisation to biodegradation, i.e. they are resistant to biodegradation and the action of light does not make them biodegradable (Obernosterer and Benner, 2004). Sunlight and especially ultraviolet radiation will oxidise DOC to CO_2 and CO as well as lower weight molecular organic compounds. Rates of photodecomposition in the field are generally reported for long residence time systems, e.g. lakes (Kopacek et al., 2003) or estuaries (Moran et al., 2000): rates of approximately, 9×10^{-3} – 0.4 mg C/l/day have been reported in lakes (e.g. Graneli et al., 1996). Photodecomposition can be catalysed by the presence of other chemical species, especially Fe, and cannot be considered independent of biodegradation (e.g. Anesio et al., 2005). Flocculation with Fe and Al can remove DOC from solution (Sharp et al., 2006) or at least facilitate photoaggregation (Maurice et al., 2002). Peat-hosted streams, which are such significant sources of DOC (Aitkenhead et al., 2007), tend to be acidic, and although generally low in ionic strength this can permit Fe and Al to be mobilised, with a consequential potential for flocculation and as steam pH rises through a catchment causing Fe and Al-oxyhydroxides to precipitate out of solution; McKnight et al. (1992) showed that such mixing of streams resulted in an average 40% removal of DOC. Equally, the solubility of DOC increases with increasing pH (Lumsden et al., 2001; Evans et al., 2012) and so DOC could desorb from POC if stream pH increased across a catchment. The work that has been done has mostly concentrated on 'old' DOC and biodegradation, and has looked at the efflux of CO_2 rather than the decrease in DOC concentrations (e.g. Algesten et al., 2004) and in systems where the residence time of the water would be months (e.g. lakes), rather than hours and days as is the case in rivers.

Several attempts have been made to quantify the loss of DOC across a catchment. Worrall et al. (2006) used a mass balance approach to calculate the DOC export at a range of

scales to show an average net loss of 40% of DOC from source to outlet across an 818 km^2 catchment. Worrall et al. (2007) used nationally-collected monitoring data for biochemical oxygen demand (BOD) as a measure of DOC turnover and found an average 31% loss across the UK fluvial network – equivalent to an additional release of 1 tonne C/km^2/yr across the entire UK land surface. However, in basing their approach upon BOD data a fixed fluvial residence time of 5 days was assumed – a long residence time for the short, relatively-unimpounded rivers of the UK (although in the peatland areas surface water storage in reservoirs is more common). What is more, BOD tends to be measured low down in the fluvial network and away from sources of fresh more readily degraded DOC. Alternatively, Worrall et al. (2012) used empirical and structural modelling of the DOC export from over 194 catchments across the UK, across 7 years and in comparison to the soil, land-use and hydro-climatic characteristics of each catchment to assess net watershed losses. A net watershed loss of DOC up to 78% was found, equivalent to between 9.0 and 12.7 tonnes C/km^2 of UK land area/yr. These figures are comparatively large when compared to other studies and did not include actual DOC measurements. Wickland et al. (2007) observed measured 6-15% conversion of pore-water DOC to CO_2, and 10-90% conversion of the vegetation-derived DOC, during one-month dark incubations, and del Georgio and Pace (2008) measured rates of loss as low as 0.4%/day, but again for dark incubations of fluvial DOC. The latter study was also for samples from near the tidal limit of the Hudson River, i.e. samples that would already have been in the river for many days. Jonsson et al. (2007) estimated that around 50% of terrestrially-derived organic carbon was mineralised but for a lake catchment where residence times would be long relative to the UK. Dawson et al. (2001) did consider a short river reach (2 km) in a peat headwater and estimated that 12-18% of DOC was removed. Wallin et al. (2013) considered a 67km^2 boreal catchment and found that CO_2 evasion from the streams represented 53% of the flux of carbon in the streams, some of

this CO_2 evasion would be due to rapid turnover of DOC in low order streams. So the objectives of this study were to: measure the loss of DOC from source to sea along a short residence time river system (rather than in a long residence-time lake which receive DOC that may be several days old and so already refractory); assess the controls on DOC degradation and loss; and thus estimate the extent of loss of DOC across a catchment.

Approach and Methodology

This study conducted in situ degradation measurements of DOC from the headwater to the former tidal limit of a major UK river, the Tees, whose headwaters are peat-covered and where DOC fluxes have been extensively studied (e.g. Worrall et al., 2008). The in-situ experiments were conducted so that it was possible to measure total loss of DOC; loss of DOC in darkness (and therefore by difference the loss due to photolytic processes); and the rate of each of these processes. Results from degradation experiments were used to construct empirical rate laws that were combined with a time series of headwater DOC concentration and estimates of in-stream residence times so that estimates of total DOC loss from the catchment could be made.

Study sites

This study considers four sites along the River Tees, northern England (Figure 2 – Table 1). The River Tees flows 132 km from its source at Moor House National Nature Reserve, before draining in to the North Sea, although the estuary is cut off by a total exclusion tidal barrage. Four sites were chosen from upstream of the barrage that differed by almost orders of magnitude in their upstream catchment area, each of which was co-located with a river flow gauging station. The two lowest order stream sites (CHS and TB – Table 1) are within the Moor House National Nature Reserve (NNR), the most extensively studied of all UK

149 peatlands (Billett et al., 2010), with 100% and 90% deep peat cover within their respective
150 catchments. The Moor House NNR is part of the Environmental Change Network (ECN)
151 monitoring programme which means that DOC concentration has been monitored in the
152 streamwater at these sites weekly since 1993 (Worrall et al., 2009). Equally, the most
153 downstream site (Broken Scar, DBS) is co-located with a water treatment works where water
154 colour (not DOC concentration) has been measured daily since 1970 (Worrall et al., 2008).
155
156 ***Degradation measurement***
157 The degradation measurements were made outside of the laboratory in ambient light and
158 temperature conditions (rather than indoors under artificially controlled conditions). The
159 study considered degradation in light and dark so as to distinguish between possible
160 components of degradation (eg. photo-induced degradation), and measured degradation over
161 timescales relevant to river residence times. Experiments were conducted each month on each
162 site over the course of a year in order to experience a range of both meteorological conditions
163 and DOC concentrations and compositions. The samples were not pre-filtered to exclude
164 particulates, because this meant that the study considered the net fate of DOC and could
165 include production from POC or adsorption by it.
166 Water samples were taken on a monthly basis from the 4 sites on the River Tees
167 (Table 1). December and January samples were only obtained from two sites; poor weather
168 conditions prevented the two sites within the Moor House NNR from being visited. Each
169 degradation experiment spanned 10 days with sacrificial sampling taking place on day 0, 1, 2,
170 5 and 10, and light and dark treatments for each site. Replicates were included within each
171 degradation experiment and over the course of the year all combination of factors were
172 replicated. No day 0 samples were replicated, but 44% of all other measurements were
173 replicates (285 of 646 samples). Replication was limited by practical constraints of the

number of quartz tubes available and the time taken to process DOC analysis. The water was then poured in to acid-washed, quartz glass tubes, stoppered with a rubber bung at the bottom, and loosely stoppered at the top. Quartz glass allows all light wavelengths to pass through it. Dark samples were wrapped in foil to prevent exposure to light. All samples were put outside in trays, with all tubes lying at an angle to prevent rainfall entering and the sample evaporating or pouring out. The angling of the tubes also stopped the light samples being shaded by the top bung and exposed a larger surface area of water to light. The samples were moved to different positions daily to avoid any bias in shading from nearby trees.

A data logger with a PAR (photosynthetically active radiation) meter and thermocouple recorded the radiation levels and air temperature at 15 minute intervals throughout the 10 day period of each month's experiment. Radiation and temperature conditions were summarised as the average conditions over the period for each sample and PAR measurements were summed to give the total radiation experienced by a sample. These were treated in this way because a sample after 10 days may have experienced the same average radiation as a sample after 1 day but will have received a larger total radiation dose. By including radiation and temperature variables it was possible to estimate the apparent quantum yield and the activation energy for DOC photodegradation.

Sample analysis

Upon each day of sampling the respective quartz tube for each site, each treatment and replicates, where appropriate, were sacrificially sampled and sub-samples frozen for subsequent analysis for DOC concentration: it is assumed that the freezing and thawing of samples did not alter DOC concentrations. Samples for DOC analysis were defrosted and filtered to 0.45 µm and the DOC concentration measured using the wet oxidation method

described in Bartlett and Ross (1988). DOC concentrations were calibrated using standards of oxalic acid with known concentrations, and only calibration curves with an R^2 of 0.95 or above were used. The Bartlett and Ross method is accurate between 2 and 60 mg/l DOC and samples were diluted so as to be within this range. Samples with a higher DOC concentration were diluted using deionised water which was also used as a blank. Absorbance at 400, 465 and 665 nm was measured and the 'E4:E6' ratio (abs at 465 nm/ abs at 665 nm) recorded. Absorbance at 400 nm is a basic (visible) colour reading and the specific visible light absorbance was taken as the absorbance at 400nm divided by the DOC concentration of the sample. The E4/E6 ratio is a measure of DOC composition, with higher ratios indicating a greater degree of humification (Thurman, 1985). All optical measurements were performed using a UV-Vis spectrophotometer, with a 1 cm cuvette. Blanks of deionised water were used.

Suspended sediment concentration in each monthly experiment was measured in samples on day 0 and day 10. Samples were filtered through pre-weighed, 0.45 μm glass fibre filters; dried to 105^{o}C and the filter paper re-weighed to give the concentration of particulate matter. The composition of the particulate matter was not analysed and particulate concentrations were only measured in a sample of 50 ml volume.

A number of additional water analyses were performed in order to provide covariate information. Alkalinity or acidity was measured by titration on day 0 and day 10. An acidity or alkalinity titration was carried out (in the field on day 0), titrating 20 ml of river water against either 0.1 M sodium hydroxide (NaOH) or 0.005 M hydrochloric acid (HCl), using five drops of phenolphthalein or bromophenol blue, respectively, as chemical indicators of pH change. Three titrations were carried out for each site and treatment, and the average volume of acid/alkali used was recorded. Conductivity, pH, and water temperature of samples as it left each quartz glass vial were measured by electrode methods. Ion Chromatography

224 was used to measure the concentrations of certain anions: fluoride, bromide, chloride, nitrate,
225 phosphate and sulphate. Cations such as Fe and Al were not included in the analysis.
226 However, the stream water at Cottage Hill Sike is regularly sampled as part of the monitoring
227 programme of the Environmental Change Network (www.ecn.ac.uk – Sykes and Lane, 1996).

228 The concentrations of DOC and the specific absorbance were analysed in both
229 absolute and relative terms where the relative value for each sample in an experiment was
230 expressed as the ratio of the measured value to measurement on day 0 for the same
231 experimental run.

232

233 ***Statistical methodology***

234 The design of the experiment incorporates four factors: month, sample day, site and
235 treatment. Each factor has a number of levels: month has 12 levels (one for each calendar
236 month): sample day has 5 levels (days 0, 1, 2, 5 and 10); site has 4 levels (CHS, TB, MIT and
237 DBS); and treatment has 2 levels (light and dark).

238 An analysis of variance (ANOVA) was used to assess the significance of all four
239 factors and where possible the interactions between the factors were also determined.
240 Furthermore, the analysis was repeated including covariates (ANCOVA). The covariates
241 were: pH, conductivity, absorbance at 400 nm, E4:E6 ratio; anion concentrations; and light
242 and temperature variables. The instantaneous river flow at the time of sampling was not
243 available to the study. The ANOVA and ANCOVA were performed separately so as to
244 explore what effects existed and whether they could be explained by the available covariates.
245 The magnitude of the effects, in this case generalized ω^2 (Olejnik and Algina, 2003), of each
246 significant factor and interaction were calculated. Post-hoc testing of the results was made
247 for pairwise comparisons between factor levels using the Tukey test in order to assess where
248 significant differences lay. There are several assumptions associated with using the ANOVA

249 approach. Firstly, the Levene test was used to assess homogeneity of variance with respect to
250 the factors in ANOVA; if this test failed then data were log-transformed. It should be noted
251 that ANOVA is robust against the assumptions of homogeneity of variance and normality of
252 the data. Secondly, the Anderson-Darling test was used to ensure that the data were
253 normally distributed; if not the data were log-transformed. Thirdly, to avoid type I errors all
254 probability values are given even if significance was assessed at the 95% level.
255
256 ***Empirical Modelling***
257 The statistical analysis was used to direct the development of empirical models of DOC loss.
258 Multiple linear regression was used to develop the empirical model based upon terms
259 identified from the ANOVA and including interaction terms. Only variables whose effect was
260 significant at least at 95% probability of not being zero were included in the developed model
261 with the further caveat that final models were also chosen so as to be physically interpretable.
262 The month factor was transformed into the sinusoidal function ($sin\left(\frac{m\pi}{6}\right) + cos\left(\frac{m\pi}{6}\right)$) where
263 m is the month number (January = 1 to December = 12). Some of the variables were
264 transformed for the sake of physical-interpretability, e.g. reciprocal of the absolute
265 temperature. When statistically significant multiple regression equations were derived a
266 partial regression analysis was performed to assess the importance of each significant term.
267 The modelling of net catchment losses required an estimate of the in-stream
268 residence, and therefore this study used the approach of Worrall et al. (2013) in order to
269 calculate the in-stream residence time from source to a monitoring point lower in the
270 catchment.
271 Flow records were available from 5 gauging stations throughout the River Tees
272 catchment and the record from the gauge furthest upstream and within a peat covered
273 catchment was used (Trout Beck – Figure 2). So as to coincide with available stream DOC

monitoring records, flows from 1994 to 2009 were considered. The in-stream residence time can be defined as the time that river water takes to transit from the point it entered the river to the point of interest (i.e. the point of monitoring):

$$t_r = \int_{x_e}^{x_m} \frac{l}{v} dx \qquad \text{(i)}$$

where: t_r = the in-stream residence time; v = the cross-sectional average river velocity; x_m = the distance of the monitoring along the river from its source above the Trout Beck gauging station; and x_e = the expected length of the river for the monitoring point m, i.e. the length along the river at which all water at monitoring point can be assumed to have entered.

The mean velocity of a river at any point can be estimated from Manning's equation (Manning, 1891):

$$v = \left(\frac{1}{n}\right)\left(\frac{A}{p}\right)^{\frac{2}{3}} s^{\frac{1}{2}} \qquad \text{(ii)}$$

where: A = cross-sectional area of the river at point x; p = the wetted perimeter; s = the water surface slope; and n = the Manning's *n* coefficient. If equation (ii) is expressed in terms of x, i.e. distance along the river, then equation (i) can be solved.

It is common for the longitudinal slope profile of a river to be expressed as an exponential function of river length using the Putzinger equation (Putzinger 1919):

$$S_x = S_0 e^{-\varphi x} \qquad \text{(iii)}$$

297 Where: S_x = the bed slope at point x; S_0 = the bed slope at source; and φ = an empirical
298 constant. It was assumed that bed slope was an approximation for the water surface slope in
299 equation (ix).
300 If it is assumed that the river has a rectangular cross-sectional area then:
301
302 $$\frac{A}{p} = \frac{dw}{(2d+w)} \quad \text{(iv)}$$
303
304 Where: d = river depth and w = river width. For a rectangular cross-section, the width of the
305 river does not vary with discharge and so it is only necessary to find an expression for river
306 depth change with river length. A rectangular section is the simplest possible section that we
307 could consider and if justified it would be possible to replace this with a more complex
308 representation of the channel cross-section. Dangerfield (1999) lists the bankfull width of 124
309 UK rivers and these data were augmented with observations from the 5 gauging stations on
310 the River Tees (Figure 2); the River Tees was not part of the original data set from
311 Dangerfield (1999). The data set of Dangerfield (1999) does not consider catchments less
312 than 13 km^2; this can only be marginally improved with data from the Tees to 11.4 km^2
313 (Table 1) The evidence shows a significant linear correlation between river length and river
314 width for catchments up to 11.4 km^2 (5 km river length) but this equation suggested that
315 rivers would be over 7m wide at source. In order to correct for this overestimation in small
316 catchments, the following was assumed based upon observations of width from the test
317 catchment used in this study:
318
319 For catchment area (C) > 11 km^2
320
321 $$w = 0.055C + 7.8 \quad r^2 = 0.61, n= 129 \quad \text{(v)}$$

For catchment area (C) < 11 km^2

$$w = 0.68C + w_0 \qquad \text{(vi)}$$

Where: C = catchment area (km^2); and w_0 = river width at source (m). A river will have finite width at source and as a default a value of 0.1 m was assumed here.

River depth varies with flow and we propose the following form of equation based upon observed depth frequency curves:

$$^{f}d_x = {}^{f}d_m - \beta e^{\left(\frac{x}{\gamma}\right)^{\delta}} \qquad \text{(vii)}$$

where: $^{f}d_x$ = depth at exceedance flow f (e.g. 10% exceedance) at river length x (m); $^{f}d_m$ = depth of the river at the monitoring point m for exceedance flow f; and β, γ, δ = empirical constants where β approximates to $^{f}d_m - {}^{f}d_0$.

The above approach was calibrated for the River Tees given data readily available for gauging stations in the UK as reported within the National River Flow Archive (www.nrfa.ac.uk) and the Flood Studies Report (NERC, 1975 - Table 2). The calibration of the above equations for the River Tees is discussed in Worrall et al. (2013). For Equation (iii) r^2 = 0.93 and for Equation (vii) the root mean square error was 0.02%, i.e. the fit of this approach was excellent and limited any error in transit time prediction. The source of most of the DOC within the River Tees is in the headwaters associated with peat soils (Aitkenhead et al., 2007). A soil map of the Tees catchment shows that peat soils end at 10 km from the source along the main river length, approximately at the location of the Trout Beck gauging

346 station, and so the in-stream residence time at this point was calculated using an intermediate
347 river length of 5 km, i.e. on average DOC enters halfway between the beginning of the stream
348 and 10 km downstream

349 Monitoring of stream water DOC concentration in the catchment headwaters was
350 weekly, and so observed concentrations were paired with the flow measurement for the same
351 time at the Trout beck, and then in-stream residence time calculated for that flow. Given the
352 in-stream residence time for a given initial concentration of DOC it was possible to calculate
353 the export from the DOC source and the expected loss to tidal limit of the study river, i.e. the
354 point at which the river enters the estuary.

355

356 **Results and Discussion**

357 It was possible to generate a sample size of 690 DOC concentrations with complete covariate
358 information and within the context of the factorial design. Summary of the water chemistry at
359 the two sites at the extremes of the study catchment over the 10 days of the study period in
360 daylight conditions is given in Table 3. The Fe and Al concentrations for the headwater
361 stream are below those reported for photoaggregation by Maurice et al. (2002).

362

363 ***DOC concentrations***

364 For nearly every month of measurement the DOC concentration in both treatments decreased.
365 The average DOC concentration over time over all sites showed a steep initial decline,
366 although the rate of decline was still not zero after 10 days (Figure 3) suggesting that further
367 decreases would have occurred in the experiments had continued for longer. The average
368 decline in DOC concentration across all months for all sites for samples in daylight was from
369 51 to 14 mg C/l after 10 days: when concentrations were judged relative to the day 0
370 concentration at each site then the average decline over 10 days was 76%. For experiments

371 only in the dark the average decline over a 10 day period was 47%. The average difference
372 across all sites and all times between samples in light and dark was 11.8 mg C/l with day 10
373 DOC concentrations of samples kept in the light being on average 29% lower than those kept
374 in the dark when judged relative to the DOC concentration on day 0. Larson et al. (2007)
375 compared DOC concentrations in samples of stream water kept in light and dark conditions
376 for 24 hours of normal sunlight and found an average decrease between 5 and 10%.

377 Of all the experiments run, there were 66 samples (out of a total of 690 samples)
378 where an increase in DOC concentration was observed. In 14 of the cases there was a higher
379 day 10 DOC concentration than day 0. Given that no raw water samples were filtered prior to
380 inclusion in the experiment it was possible that particles or the microbial population within
381 the sample generated DOC over the course of the experiments. Samples where there was an
382 increase in DOC over the course of the experiment were not removed from the analysis.

383

384 ***ANOVA on DOC concentrations***

385 The Anderson-Darling test showed that neither the distribution of DOC concentration nor
386 relative DOC concentration for the experiments conducted in the light and those in the dark
387 met the condition of normality, but therefore all subsequent ANOVA were performed on log-
388 transformed data which did exhibit a normal distribution. Conversely, the Anderson-Darling
389 test of the photo-induced degradation data (i.e. the difference in concentration between
390 experiments performed in the light and dark) was normally distributed and so this not
391 transformed further.

392 When the relative concentration data for all treatments (daylight and dark) were
393 considered without covariates, all single factors were found to be significant (Table 4). The
394 least important single factor was Site (explaining only 0.4% of the variance in the original
395 dataset). One of the reasons for using relative DOC concentration was to minimise the

difference between sites, and so this result indicates that this was largely effective. Post-hoc testing showed that the difference between sites was largely associated with the difference between the CHS and MIT, but not between CHS and DBS. There were no significant interactions between the Site factor and any other factor. The most important factor was Day, i.e. the time over the experiment with all days being significantly different from each other. The second most important factor was the difference between treatments, with the relative DOC concentration in the light being 48% lower than those kept in the dark. Indeed the most important interaction was that between Day and Treatment factors which reflects the difference in the curves illustrated in Fig. 3. There was a significant effect due to month but this may reflect the importance of the Day0 concentration for the degradation rate (with faster degradation rates associated with higher initial concentrations) rather than a seasonal cycle in degradation behaviour per se, which also explains the significant interactions between the Month factor and the Day and the Treatment factors. Overall the ANOVA of the relative DOC concentration explains 62.7% of the variance in the original data, i.e. the error term represents 37.3% of the variance. This error term represents the unexplained variance which was not only due to sampling or measurement error but also variables, factors or their interactions that were not or could not be included: inclusion of covariates should decrease this term.

Inclusion of covariates into the ANOVA did increase the proportion of the variance explained, by 4% (Table 4). However inclusion of covariates did not make any of the factors or interactions insignificant; on the contrary, inclusions of significant covariates increased the importance of the differences between sites even when relative DOC concentration was being tested. The most important covariate was the specific absorbance, which significantly declined with increasing DOC concentration. The second most important covariate was the day0 concentration, where relative concentration declined faster with increasing day0

concentration. This suggests that degradation rate was concentration dependent. No other covariates were found to be significant. No other covariates were found to be significant in this analysis.

Guided by the results of the results of the ANOVA it was possible to give the best-fit equation for the change in the DOC concentration (ΔDOC):

$$ln(\Delta DOC) = 1.05\ln(\mathrm{day}_0) + 0.28\ln t - 0.29\left(\sin\left(\frac{\pi m}{6}\right) + \cos\left(\frac{\pi m}{6}\right)\right) - 1.15 \qquad \text{(viii)}$$

$r^2 = 0.76$, n = 264

(0.04) (0.04) (0.05) (0.18)

where: day_0 = the DOC concentration on day zero of each experiment (mg C/l); t = time since the start of the experiment (days); m = month number (January = 1 to December = 12). Only variables that were found to be significant different from zero at least at a probability of 95% were included. The values in brackets give the standard errors on the coefficients and the constant term. The partial regression analysis shows that the most important variable is ln(day0) (partial regression coefficient = 0.66) with the other terms of approximately equal importance.

ANOVA on Photo- induced degradation

The difference between the dark and light concentrations in each experiment was taken as the estimate of the impact of photic processes. The extent of photo- induced degradation could be estimated in 313 cases and the loss due to photo-induced degradation varied from 48 mg C/l and -11 mg C/l (i.e. as above in some experiments the DOC concentration was observed to increase, implying photo-induced production). The ANOVA shows that all single factors were significant but that there were no significant interactions

between those factors (Table 5). Only one variable, and no others, was found to be a significant covariate - the day_0 concentration. The Month factor, although significant, shows no clear seasonal cycle which may imply that hydroclimatic conditions on the day of sampling (e.g. riverflow) are more important than the season of the year. The Day factor showed a significant maximum in the difference due to photo-induced degradation after 2 days (Figure 4, also apparent in Figure 3) which then declines to the 10 day period.

Given the results of the ANOVA it was possible to identify the best-fit equation for the loss due to photo-induced degradation (ΔDOC_{photo}):

$$\Delta DOC_{photo} = 35.2 + 0.47[DOC] - 13.4ln[DOC] - 933\frac{Abs_{400}}{[DOC]} \quad \text{(ix)}$$

$r^2 = 0.52$, n=313

(9.0) (0.06) (3.0) (255)

Where: [DOC] = the DOC concentration (mg C/l); and Abs_{400} – absorbance at 400nm. The most important term in Equation (ix) is ln[DOC] with a partial regression coefficient = 0.69, followed by Abs400/[DOC] with the least important term being [DOC] having a partial regression coefficient = 0.035.

It should be noted that neither temperature nor PAR variables were found to be significant covariates in any of the above approaches. However, it was possible to estimate the apparent quantum yield (AQY) in 158 of the experiments and this was found to vary between 9.6 and -1.7 mmol C/mol photons (again there were periods of photo-induced production as opposed to photo-induced degradation) – on an energy basis this equates to a maximum AQY of 1.9 mg CO_2/kJ. Most values of AQY in the literature are defined for single wavelengths (eg. Boyle et al., 2009) or for inappropriate end-products making them less transferrable to this study (eg. Stubbins et al., 2010). Osborn et al. (2009) measured AQY

for DOC values between 1 and 3 mmol C/mol photons, for samples at the mouth of the Mackenzie River (> 180,0000 km^2). Soumis et al. (2007) give photoreactivity of DOC in sterile lake water as between 15.5 and 35.8 mg CO_2/kJ. This larger photoreactivity may be due to the experiment being performed in sterile containers that remove any biotic process and so photic processes are the only process operating. The ANOVA of the AQY showed significant effects due to Day, Month and with day_0 as a covariate. Month was the most important factor with a peak in December and a minimum between February and June. This suggests that some months were associated with proportionately more photo-induced production than other months. This seasonal cycle could appear to be the inverse of the day length or solar declination, both of which would have peaked in June rather than December when the days are shortest and the sun's declination to the horizon at its lowest. It should be remembered that AQY is a measure of the photo-induced degradability and not the amount of photo-induced degradation, i.e. the DOC in December was more photodegradable.

Rate of Degradation

The rate of degradation of DOC was considered relative to the individual treatments, i.e. i) the rate of degradation in the light (i.e. total degradation); ii) the rate of degradation in the dark; and iii) the difference between the two treatments which was taken as the rate of photic processes. For samples in the light, the degradation rate varied from 30.1 mg C/l/day to -3.5 mg C/l/day, i.e. increases or no change in DOC concentrations were observed in 60 cases.

Rate of Degradation in the light

The ANOVA of the rate of degradation for samples in the light showed that all factors were significant (Table 6). When no covariates were included then all 3 factors were found to be significant (obviously no treatment factor was included because only experiments in the

light were being considered). Once covariates were included then neither Site nor Month factors were found to be significant. The lack of significance for the Site factor means that this study found that the different parts of the river did not have inherently different degradation rates. Equally, the lack of a significant difference between months of sampling suggests that there is no seasonal cycle in degradability. When covariates were included then both $\ln(day_0)$ and 1/Temp were found to be significant and no others, although collectively they explained only 8% of the original variance. Given the results of the ANOVA the best fit equation for degradation rate in daylight was:

$$\ln(rate_{light}) = 13.5 + 0.74ln(day_0) - 1.28lnt - \frac{3824}{T} \quad \text{(xi)}$$

$r^2 = 0.61$, n = 167

(5.7) (0.12) (0.1) (1567)

Where: T = absolute temperature of the experiment (K). The residuals of equation (xi) were normally distributed. The most important term in Equation (xi) is $\ln(day_0)$ with a partial regression coefficient =0.51 and the least important term being 1/T with a partial regression coefficient = 0.035. Although the visual inspection of the residuals of equation (x) show no obvious changes, the main effects plot of $\ln(rate_{light})$ vs t (Figure 5) would suggest that, although a straight line fit was significant, a combination of two straight lines would be better, with one fast rate equation covering the period up to approximately 4-5 days and one after 5 days. The significance of the reciprocal of absolute temperature in equation (xi) means that it was possible to estimate the activation energy of the degradation given a value of the universal gas constant as 0.692Jj/K/gC and in which case this would be 2.6 ± 1.2 kJ/gC.

Rate of degradation in the dark

It was possible to calculate the rate of degradation in the dark in 258 experiments, which ranged from a decrease of 19.4 mg C/l/day to -6 mg C/l/day, i.e. increase or no change in DOC concentrations were observed in 77 cases. For the rate of degradation in the dark the ANOVA shows that all factors were significant (Table 7). Once covariates were included then site was found not to be significant, however, unlike when considering the rate of the reaction in the light there was still a significant role for the month factor, i.e. there was a seasonal cycle in aphotic degradability. The main effects plot of the month factor shows that degradability peaked in July and October at 6.11 mg C/l/day, and was at a minimum in November at 0.28 mg C/l/day (Figure 6). There is a superficial similarity between the rate of degradation and the annual average temperature during each month's experiment but the temperature did not show the local maxima in July and October. When covariates were included then both $\ln(day_0)$ and 1/Temp were again found to be significant: no others were found to be significant

Given the results of the ANOVA the best fit equation for degradation rate in darkness was:

$$ln(rate_{dark}) = 0.71\ln(day_0) - 0.7\ln t - 0.42\sin\left(\frac{\pi m}{6}\right) - 0.59\cos\left(\frac{\pi m}{6}\right) + \frac{3267}{T} \quad \text{(xii)}$$

$r^2 = 0.45$, n = 178

(0.11) (0.10) (0.17) (0.20) (2783)

where all terms are defined as above. The residuals of equation (xii) were normally distributed. The most important term in Equation (xii) is ln(day) with a partial regression coefficient = 0.29 and the least important term being 1/T with a partial regression coefficient = 0.008. As above the main effects plot of $\ln(rate_{dark})$ vs. t suggests that a more complex rate law than a single rate law. Again it was possible to estimate the activation energy of the

546 degradation and in which case this would be 2.3 ± 1.8 kJ/gC, i.e. not significantly different
547 from the estimate based on the degradation rate in the light. It is difficult to find studies that
548 measure activation energy in comparative systems, but Alperin et al. (1995) give a value of
549 6.7 kJ/gC for DOC in marine sediments; a higher value may be expected for DOC that is
550 likely to have been older and more recalcitrant than that found in rivers.
551
552 ***The rate of photo-induced degradation***
553 The rate of the photo-induced degradation could be calculated from 168 experiments
554 and varied from 27.3 mg C/l/day to -4.3 mg C/l/day, i.e. in 39 cases an increase was
555 observed. All 3 factors were found to be significant but again the Site factor was not found to
556 be significant when covariates were included (Table 8). As before the Day factor was found
557 to be the most important, though there was a significant seasonal cycle where the rate peaked
558 in September at 7.7 mg C/l/day with a minimum in June at 1.1 mg C/l/day. The covariates
559 found to be significant were not only Day 0 but also cumulative PAR.
560
561 $$ln(rate_{photo}) = 31.4 - 10.51\ln(day_0) - 2.02\ln t + 9.1\sin\left(\frac{\pi m}{6}\right) - 0.005\frac{\sum PAR}{t} \quad \text{(xiii)}$$
562 $r^2 = 0.29$, n = 94
563 (14.8) (4.5) (2.0) (3.9) (0.003)
564
565 Where all terms are defined as above. The significant effect of the term in $\frac{\sum PAR}{t}$ does suggest
566 that we could measure significant AQY. The most important term in Equation (xiii) WAs lnt
567 (partial regression coefficient = 0.39) with no other term having a partial regression
568 coefficient greater than 0.07. By using partial regression it was possible to examine the
569 relationship between $\ln(rate_{photo})$ and $\frac{\sum PAR}{t}$, which does suggest that the rate of photo-induced

570 degradation declined with increasing ΣPAR. This implies that there was a progressive
571 decrease in the sensitivity of remaining DOC to photo-induced degradation, i.e. that
572 photobleaching had occurred, and that this was associated not only with time but also with
573 increased light intensity.
574
575 ***Empirical modelling***
576 The estimated in-stream residence time for water between Trout Beck and the tidal limit
577 varied from 12.9 to 127.2 hours. Between 1994 and 2009 the annual flux of DOC at Cottage
578 Hill Sike varied from 14.7 to 33.3 tonnes C/km^2/yr. For each measurement of DOC
579 concentration at Cottage Hill Sike the flow measurement at the Trout Beck gauging station
580 was used to calculate the in-stream residence time. Given an initial concentration and an
581 estimate of the in-stream residence time it was possible to calculate the loss of DOC and the
582 export that would represent. Based on the in-stream residence time and equation (viii), then
583 the equivalent flux at the tidal limit would be between 5.4 and 12.6 tonnes C/km^2/yr which
584 gives an equivalent removal rate of 7.7 and 21.4 tonnes C/km^2/yr which is a removal rate of
585 between 48 and 69% (Figure 7). There was a significant trend in the DOC flux from Cottage
586 Hill Sike, which increased at average rate across the whole period of 0.59 tonnes C/km^2/yr^2
587 (3.0 % /yr^2) but no significant trend was observed for the flux at Broken Scar over the same
588 period. Therefore, it is perhaps not surprising that there was a significant increase in the
589 predicted removal rate – 0.52 tonnes C/km^2/yr^2 (5.0 %/yr^2). The increase in the predicted
590 removal rate is in line with the increase observed for the flux of DOC at source, and so
591 therefore the observations of DOC degradation for this catchment imply that the river is
592 capable of removing most or all of the increase in DOC export from the source, before it
593 reaches the sea. This in turn implies that observed increases in DOC flux from peat soils
594 across the northern hemisphere could translate into large increases in loss of CO_2 to the

595 atmosphere. However, in this case this would assume no other changes in sources in the rest
596 of the catchment such as no changes in urban or agricultural sources.
597
598 ***Limitations and Implications***
599 One particular process that this study has not quantified is the processing of the particulates.
600 We deliberately did not filter the samples prior to experiment, to allow for the possibility of
601 interaction between particulates and DOC, but because of the small volume of samples it was
602 not possible to test the composition of the particulates over the course of the experiments.
603 However, suspended sediment concentrations were measured in samples at day 0 and day 10,
604 meaning that it was possible to assess the change in particulate concentration over a 10 day
605 period in 35 cases. Over these 35 cases no increases in suspended sediment concentration
606 were observed, with removal rates ranging from 0.2 to 15.6 mg C/l/day. Without
607 compositional information it is difficult to infer the extent to which the particulate carbon
608 content has changed. However, for the CHS there is no mineral soil in the catchment and so
609 any suspended sediment can be assumed to be organic. There were 9 cases where it was
610 possible to compare the day 0 and day 10 samples at CHS, and this gave a loss of POC
611 between 7.5 to 29.4 mg C/l/day (assuming a carbon content of 45%), which is a removal rate
612 of between 38 and 87% over 10 days. Of course this assumes that our experimental set up
613 mimics the settling out of POC into a streambed, and the analysis does not indicate whether
614 the POC was converted to directly to CO_2 or to DOC. Nevertheless, the absence of any
615 evidence of increasing particulate concentrations in any of the experiments argues strongly
616 that the widespread reductions in DOC observed were not due to flocculation or precipitation.
617 Based on BOD measurements from rivers across England and Wales, Worrall et al.
618 (2007) estimated an average 29% removal of DOC, although this estimate was based upon an
619 assumption of a fixed 5 day residence time. Worrall et al. (2006) working on the River Tees

620 calculated the DOC export at a range of scales to show an average net loss of 40% of DOC
621 from source to outlet. Worrall et al. (2012) developed an empirical model of net watershed
622 loss based upon data from 169 catchments and applying the method to the Tees catchment
623 suggests a removal rate of 58%. Therefore, the estimates of removal rates are not dissimilar
624 to previous less detailed estimations, and indeed not dissimilar to estimates of global in-
625 stream removal (42% - Cole et al., 2007).

626 Worrall et al. (2012) estimated the flux of DOC from the UK was 909 ± 354 ktonnes
627 C/yr (2.2 – 5.2 tonnes C/km^2/yr), so applying the removal rates measured in this study
628 suggests that the flux of DOC at source in the UK would have been between 1067 and 4074
629 ktonnes C/yr (4.4 – 16.7 tonnes C/km^2/yr). Rates of DOC loss through the UK's fluvial
630 network would be between 512 and 2811 ktonnes C/yr (2.1 – 11.5 tonnes C/km^2/yr), which
631 represents a greenhouse gas emission of between 1880 and 10320 ktonnes CO_{2eq}/yr. Even the
632 lower of these estimates would represent 1% of the UK's national total GHG budget.

633 Although this study has been able to develop empirical rate law for the loss of DOC,
634 it is clear from this study that if we are to further understand the turnover of DOC in the
635 rivers then it will be necessary to consider changes on hourly timescales rather than daily, and
636 to better constrain in-stream residence times across regions. The study suggests that there is a
637 strong influence of radiation on the loss of DOC which would create a strong diurnal cycle in
638 the loss or processing of DOC, which in the short residence times of rivers has two
639 implications: firstly, that without a good knowledge of in-stream residence time it will be
640 difficult to judge how much DOC is lost. Second, a strong diurnal cycle in northern latitudes
641 also implies that there should be a strong annual cycle in loss of DOC, even with a fixed in-
642 stream residence time. The study suggests that there at least two broad types of DOC, with
643 one rapidly turning over into the other, at the same time as the particulate organic matter is

644 itself turning over producing DOC. The interplay of at least these three processes means that
645 we need to consider each of these on sub-daily timescales.
646
647 **Conclusions**
648 The study has found that for peat-derived DOC in the river network the average loss of DOC
649 in light conditions was 73% over a 10 day period, but with the majority of the loss occurring
650 in the first 2 days. When extrapolated across a catchment the annualised removal rate was
651 between 48 and 69% of the flux of DOC at its soil source. These measured removal rates are
652 for DOC close to its source in rivers with residence times of only several days, and not for
653 longer residence times systems or for the relative old DOC found downstream in a larger
654 river networks. The results suggest that rivers could be sources of CO_2 equivalent to several
655 percent of a national GHG inventory.
656
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660
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Figure 1. Schematic diagram of the DOC processing within a peat-sourced stream

Figure 2. Location of the study catchment with monitoring sampling points and river flow gauging stations used within the study.

Figure 3. The main effects plot of DOC concentration change for light and dark over the period allowed in the study. Error bar is given as the standard error but smaller than symbol size.

Figure 4. The main effects plot of the change in loss due to photo-induced degradation over the course of the experiment. Error bar is given as the standard error.

Figure 5. Main effects plot of rate of DOC loss in light conditions over time in the experiment. Error bar is given as the standard error.

Figure 6. Main effects plot of the seasonal cycle in the rate of DOC loss in light conditions over time in the experiment (1 = January, 12= December) in comparison to the average air temperature during each month's experimentError bar is given as the standard error.

Figure 7. The estimated export of DOC at the peat source (Cottage Hill Sike) in comparison to the estimated areal loss of DOC and therefore the expected DOC export at the tidal limit.

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